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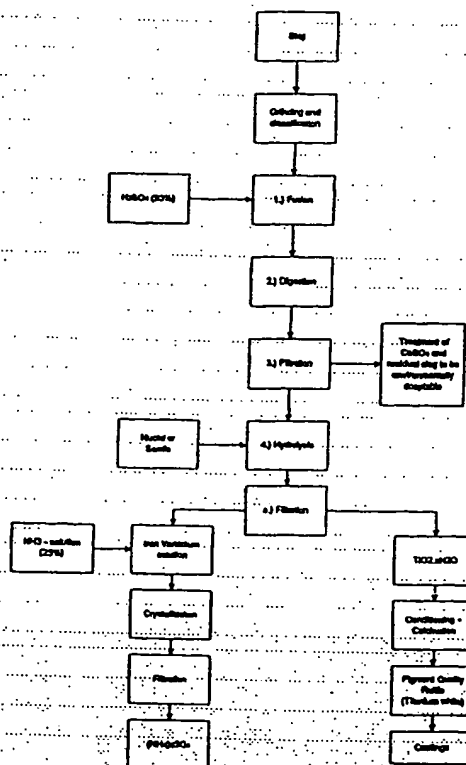
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(54) Title: RECOVERY OF TITANIUM DIOXIDE FROM TITANIUM OXIDE BEARING MATERIALS LIKE STEELMAKING
SLAGS

(57) Abstract: A method of recovering titanium dioxide from a titanium oxide bearing raw material, such as e.g. steel slags rich in TiO₂ includes the steps of grinding the titanium dioxide raw material, reacting the particulate raw feed material with sulphuric acid under specified conditions, digesting and filtering the resultant cake material containing titanyl sulphate, hydrolysing the titanyl sulphate and, after washing the hydrolysate, calcining the hydrolysate to produce titanium dioxide.



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RECOVERY OF TITANIUM DIOXIDE FROM TITANIUM OXIDE BEARING MATERIALS LIKE STEELMAKING SLAGS

BACKGROUND OF THE INVENTION

THIS invention relates to the recovery of titanium from titanium bearing materials, and in particular to a method of recovering titanium dioxide or titanium metal from a titanium dioxide bearing material.

Highveld Steel and Vanadium Corporation is a large manufacturer of steel using its own unique steel manufacturing process. The slag produced in this steel manufacturing process is rich in titanium dioxide, typically in amounts of 22 to 32% of the slag material.

Pure titanium dioxide is white in colour and is, therefore, a valuable pigment used in many applications such as the production of paints, paper, cement, polymers and the like. The slag produced in the Highveld Steel manufacturing process is an ideal source of titanium dioxide for this purpose. However, there is currently no viable commercial process for recovering the titanium dioxide from the slag material.

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- g) filtering the hydrolysate followed by washing with sodium hydroxide, ammonium hydroxide, water, phosphoric acid and/or diluted sulphuric acid; and
- h) calcining the hydrolysate to drive off any residual acid and water of crystallisation to produce titanium dioxide.

The slag in step a) is preferably ground to form a particulate material in which at least 80% of the particles are able to pass through a 175 micron mesh, more preferably a 45 micron mesh.

The reaction of the sulphuric acid solution and particulate feed material in step b) typically takes place in a fusion reactor, which may be a batch or continuous fusion reactor.

The temperature is preferably raised in the fusion reactor by introducing pre-heated air into the reaction vessel.

Cold air is preferably blown through the cake material, in particular for a period of about 4 hours, after the reaction is completed to produce a porous cake.

The porous cake is preferably left to mature for an appropriate time, typically about 8 hours.

In step c), air is preferably introduced with the water, and optionally recovered process acid, in order to assist with agitation to dissolve the cake.

The air is preferably cold air to control the reaction temperature, preferably below about 85°C, more preferably below about 75°C, in order to prevent premature crystallisation of TiO_2 .

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BRIEF DESCRIPTION OF THE DRAWING

The invention will now be described in more detail, by way of example only, with reference to the accompanying drawing which is a schematic flow diagram of a preferred embodiment of a method of recovering titanium dioxide according to the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention is directed at a so-called sulphating process for recovering titanium, in particular titanium dioxide, from a titanium bearing material, in particular a slag produced in a steel manufacturing process containing titanium dioxide.

In the first embodiment of the invention, the titanium bearing material is ground to an appropriate particle size and classified. For ease of describing the process, reference is made to a slag produced in a steel manufacturing process, the slag containing about 22 to 32% titanium dioxide. The raw material is ground into a particulate material until at least 80% of the titanium dioxide in the slag is liberated and is able to pass through a 175 micron mesh, more preferably a 45 micron mesh.

The particulate material is then reacted with sulphuric acid in a continuous or batch fusion reactor. In order to carry out the reaction, the desired amount of sulphuric acid, typically a 93% to 96% sulphuric acid solution at suitable temperature, is firstly introduced into the fusion reactor. The particulate feed material is then added to the sulphuric acid solution. Preheated air, or steam if appropriate, is then introduced through the bottom of the reactor and allowed to rise through the reaction mix in order to heat the reaction mix to the point where the reaction commences. The heated air is normally introduced at about 400°C and the reaction usually commences at around 100°C.

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The dense solution is processed in a hydrolysis step in order to precipitate out the $\text{TiO}_2 \cdot x\text{H}_2\text{O}$. During this hydrolysis step, about 1% nuclei rutile is added to water at 25°C , whereafter the water is heated to a temperature of about 60°C . The titanyl sulphate solution is then added to the seeded water and the temperature raised to boiling point ($\pm 95^\circ\text{C}$), at which stage hydrolysis takes place. Hydrolysis is clearly evident from the white suspension which is produced. This step is allowed to proceed for ± 1 hour in order for hydrolysis to be completed. The hydrolysate is then filtered in a hot filtration step in order to recover the hydrated titanium dioxide. The filtration is carried out in a hot filtration step in order to keep the particle size large enough to be captured by the filtering medium.

The liquor is a misty blue colour due to the Fe and V components which can be recovered from the liquor. Once the Fe and V have been recovered, the liquor may be reused for washing or leaching.

The hydrolysate recovered in the filtration process contains $\text{TiO}_2 \cdot x\text{H}_2\text{O} \cdot \text{SO}_3$. This product is washed with an ammonium solution, typically a 12.5% NH_3 solution, to remove any residual Fe and V and also to remove sulphate as ammonium sulphate.

The resultant $\text{TiO}_2 \cdot x\text{H}_2\text{O}$ hydrolysate, containing about 91% TiO_2 , and some SO_4^{2-} , VO_2SO_4 , FeOSO_4 and FeSO_4 , is then calcined in an oxidative environment by passing air through the product at a temperature of about 950°C for about an hour. The SO_3 is driven off and can be recovered as H_2SO_4 together with the waters of crystallisation. The resultant titanium dioxide product has a purity of about 98%.

If desired, the leachate containing the VO_2SO_4 and $\text{FeOSO}_4/\text{FeSO}_4$ is crystallised, and filtered to recover $(\text{NH}_4)_2\text{SO}_4$ fertiliser. The solution containing

with reference to the following non-limiting example.

EXAMPLE

The slag used in this example comprised the following components:

CaO	14%
MgO	13%
SiO ₂	25%
Al ₂ O ₃	15%
S	0,3%
TiO ₂	25%
V ₂ O ₅	0,7%
FeO	6,5%

The raw slag material was ground and classified until 80% of the fine particulate material had an average diameter of less than 175 microns, as determined by passing the particulate material through a 175 micron mesh.

15 Litres of 93% H₂SO₄ was introduced at 25°C into a sealed reactor. 20 kg of fine slag material was then introduced into the reactor and after about 2 minutes the temperature rose from about 25°C to about 63°C, which is indicative of the exothermic reaction already taking place. Air, which had been pre-heated to 400°C, was then introduced into the bottom of the reactor. The appropriate valve was opened to about 25% of its capacity. Within 5 minutes, the temperature of the reaction mixture had reached 100°C whereupon the exothermic reaction started to take place, as was evident from the violent white fumes of SO₃ coming off the reaction mixture. After a further 3 minutes the temperature had risen to about 173°C and continued to rise to a maximum of about 210°C, whereafter the temperature started to drop. After a further 10 minutes, the temperature had dropped to about 100°C at which time cake formation commenced. The air valve was then opened to its full capacity and the temperature once again rose to about 130°C whereafter it dropped off. The air was allowed to continue flowing through the cake mass for a period of 6 hours to form a porous cake.

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greater than 99.99% titanium dioxide from the 98% titanium dioxide material.

Although the additional purification step results in a greater than 99.99% titanium dioxide product, chlorine gas is an extremely dangerous product and has to be used under strictly controlled conditions. The applicant therefore set about adapting the process to produce 99.9% titanium dioxide without the need for an additional gas chlorination stage. It was surprisingly found that by optimising the process steps in a number of areas, a titanium dioxide product having a purity of greater than 99.9% can be obtained.

Accordingly a second, particularly preferred embodiment will now be described with reference to the accompanying drawing.

The titanium slag available is dried as needed and ground to a uniform fine particle size. The pulverized slag is mixed with approximately 1.3 parts by weight of 93% sulphuric acid and heated with pre-heated air in a reactor vessel. At about 100°C the exothermic reaction starts and the slag is converted into a solid mass composed of soluble titanium, vanadium and iron sulphates. The use of heated air instead of heated steam has been found to be preferable. The reason for this is that the Highveld Steel slag used in the process has free iron present, in an amount of about 4%, in the ferrous state. Accordingly, it is undesirable to have water in the fusion reaction as it would transform the free iron to the Fe^{+++} state. In addition, the presence of oxygen in the heated air assists in the recovery of the titanium by converting Ti^{+++} to Ti^{++++} .

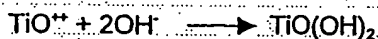
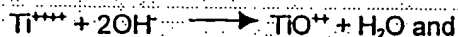
Cold air is then blown through the cake for about 4 hours after the reaction is completed to produce a porous cake. The cake so produced is left to mature for about 8 hours.

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dense yellow solution is obtained after filtering, which is rich in peroxide $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$. By way of information, the peroxide is an oxidising substance which is unstable in the presence of water and is much more soluble than TiO_2 or $\text{TiO}_2 \cdot \text{H}_2\text{O}$. It dissolves in acid solutions with the formation of yellow to red pertitanyl ions (TiO_2^{++}). In alkaline solutions, it forms titanate ions (HTiO_3^-) and/or colourless pertitanate ions (HTiO_4^- and TiO_4^{--}). The solubility of the peroxide is around 1g.mol/l at a pH of 0.5 (acid medium) and at a pH of 12 (alkaline medium). By the action of hydrogen peroxide on very acid solutions of tri- or tetravalent titanium, a solution of peroxidized TiO_2^{++} ions is obtained, which deposits as a precipitate of peroxide, $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$, upon increasing the pH.

During the hydrolysis step, the titanium solution is transformed into a white titanium oxyhydrate slurry. The steps that have gone before are fundamental in preparing the titanium compounds for hydrolysis. One step which is not required when using Highveld slag is crystallization and vacuum concentration. Thus, hydrolysis is carried out by contacting the titanyl sulphate containing solution with heated water which has been seeded with nucleating or seeding agents, in particular nuclei rutile, and then boiled.

The formation of titanyl hydroxide proceeds according to the following reactions:



To increase the rate of thermal hydrolysis of sulphate solutions at atmospheric pressure and at the same time obtain products of pigment grade, nucleating or seeding agents are added. Normally only 1% nuclei or seed agent is required.

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The main reason for washing the hydrolysate is to neutralize the liquor and to improve the crystal properties. Conditioning agents such as dilute acids and zinc or aluminium powder or a powerful non-metallic reducing agent or phosphoric acid or an alkaline metal could also be introduced during this washing stage, to ensure the formation of the rutile structure during the calcination process that follows.

The thoroughly purified and washed hydrolysate obtained by the thermal hydrolysis of titanium salt solutions is an amorphous hydrous oxide which still contains impurities as chemi-adsorbed acid. In addition, it is too fine-grained and almost amorphous, which is undesirable for pigment grade TiO_2 . In the production of pigment grade TiO_2 , accordingly, a calcination step is necessary to drive off the water and residual acid and at the same time convert the titanium dioxide to the crystalline form of a required particle size. At the same time, desired pigmentary properties are developed.

Amorphous titanic oxide or hydroxide ($\text{TiO} \cdot x\text{H}_2\text{O} \cdot \text{SO}_3$), such as is obtained from the sulphate solution, is converted to the crypto crystalline modification of pigment grade TiO_2 by calcination at 950°C for 1 hour.

Grinding, classifying and pulverizing of the calcined product produces the TiO_2 pigment material having a purity of greater than 99.9%.

The various solutions produced in a test process of the invention were analysed by Anglo American Research Laboratories (Pty) Ltd for the presence of Si, Ca, Ti, V and Fe, and the results thereof are set out in table 1 below.

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Table 2: Analysis of TiO_2

	TiO_2 %	Fe $\mu\text{g/g}$	S $\mu\text{g/g}$	V $\mu\text{g/g}$
6	99.9	413	1969	176
7	97.4	234	18817	26
9	99.9	525	446	198
10	81.3	546	65126	205

Key to table 2:

- 6. TiO_2 calcined for 1 hour.
- 7. TiO_2 calcined for $\frac{1}{2}$ hour.
- 9. TiO_2 calcined for 2 hours.
- 10. TiO_2 undergoing no calcination.

From the above table, it is evident that at least 1 hour is required for obtaining 99.9% TiO_2 . However, in order to reduce the amount of S (in the form of SO_3), 2 hours in the calcining operation was found to be optimum.

From the above results, it is evident that it is possible to obtain pigment grade titanium dioxide having a purity of 99.9% or greater without having to carry out an additional purification method.

As the process is able to produce titanium dioxide which is extremely pure, it provides an ideal means of recovering titanium dioxide from slag or other titanium dioxide bearing materials to produce white pigment or titanium metal, valuable products in industry.

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g) filtering the hydrolysate followed by washing with sodium hydroxide, ammonium hydroxide, water, phosphoric acid and/or diluted sulphuric acid; and

h) calcining the hydrolysate to drive off any residual acid and water of crystallisation to produce titanium dioxide.

2. A method according to claim 1, wherein the slag in step a) is ground to form a particulate material in which at least 80% of the particles are able to pass through a 45 micron mesh.

3. A method according to claim 1 or claim 2, wherein the reaction of the sulphuric acid solution and particulate feed material in step b) takes place in a fusion reactor.

4. A method according to claim 3, wherein the temperature is raised in the fusion reactor by introducing pre-heated air into the reaction vessel.

5. A method according to any one of claims 1 to 4, wherein cold air is blown through the cake material after the reaction is completed to produce a porous cake.

6. A method according to claim 5, wherein the cold air is blown through the cake material for about 4 hours.

7. A method according to claim 5 or claim 6, wherein the porous cake is left to mature.

8. A method according to claim 7, wherein the porous cake is left to mature for about 8 hours.

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- j) condensing the gaseous TiCl_4 to produce a crude liquid TiCl_4 ;
- k) distilling the crude liquid TiCl_4 to produce a substantially pure TiCl_4 liquid; and either
- l) gasifying the pure TiCl_4 liquid to produce gaseous TiCl_4 and oxidising the gaseous TiCl_4 to produce titanium dioxide pigment, or
- m) treating the pure TiCl_4 liquid in a conventional process to produce metallic titanium.

INTERNATIONAL SEARCH REPORT

Int'l Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B34/12 C22B7/04 C22B3/08 C01G23/047 C01G23/053

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2 589 910 A (SCHNEIDER ERWIN L) 18 March 1952 (1952-03-18) column 7, line 27 - column 8, line 15; claim 1	1,4
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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